

Magnetocaloric properties of $\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ compounds, with $x \leq 0.60$

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Abstract. In this paper the results of specific magnetization and magnetocaloric effect (MCE) measurements for $\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ system upon the Co substitution by Fe for the $x = 0 \div 0.60$ range are presented. Phase composition was controlled by X-ray diffraction analysis. MCE has been studied within the temperature range of 300-850 K in magnetic fields up to 17 kOe by the magnetic entropy change calculation (ΔS_m). It was found that in contrast to the previously studied $\text{R}(\text{Co-Fe})_2$ compounds where $\text{R} = \text{Dy}, \text{Ho}, \text{Er}$, an ordinary symmetrical peak of $\Delta S_m(T)$ in the vicinity of T_C is observed for presented samples. Additionally, the MCE comparison of $\text{Gd}(\text{Co}_{0.88}\text{Fe}_{0.12})_2$ with that for the isostructural $\text{Gd}(\text{Ni}_{0.88}\text{Fe}_{0.12})_2$ compound having a plateau-like ΔS_m temperature dependence is given. The obtained results are discussed.

1 Introduction

In the last two decades intensive research has been devoted to the search for and development of new magnetocaloric materials for the purpose of their application in energy-efficient and environment-friendly systems of magnetic cooling. Different types of compounds with large magnetocaloric effect (MCE) in a narrow temperature interval around the magnetic phase transition temperature were pointed out: RCO_2 (R – heavy rare-earth metal), $\text{Gd}_5\text{Ge}_2\text{Si}_2$, $\text{MnFe}(\text{P}_{1-x}\text{As}_x)$, $\text{La}(\text{Fe}_{13-x}\text{Si}_x)$, Ni-Mn-Ga , et al. [1]. Nevertheless, the study of the magnetic properties and the MCE in the $\text{R}(\text{Me}_{1-x}\text{Fe}_x)_2$ ($\text{R} = \text{Tb}, \text{Ho}$; $\text{Me} = \text{Al}, \text{Ni}, \text{Co}$) quasi-binary systems shown that a partial substitution of Me-element by Fe leads to Curie temperature (T_C) increase, and the emergence of significant MCE in a wide temperature range below its T_C [2-5]. The latter is an important material property when it is used for the manufacture of magnetic refrigerator working bodies.

Our recent MCE measurements for some $\text{Dy}(\text{Co}_{1-x}\text{Fe}_x)_2$ [6], $\text{Ho}(\text{Co}_{1-x}\text{Fe}_x)_2$, $\text{Er}(\text{Co}_{1-x}\text{Fe}_x)_2$ [7], and $\text{Gd}(\text{Ni}_{1-x}\text{Fe}_x)_2$ [8] compounds with Ni and Co substitution by Fe confirmed that results and allowed to suggest the reasons of MCE peak widening in the temperature range below their T_C . In general, the results obtained demonstrate a qualitatively identical picture, as in compounds of the $\text{R}(\text{Co-Fe})_2$ system with $\text{R} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$, and $\text{R}(\text{Ni-Fe})_2$ compounds with $\text{R} = \text{Gd}, \text{Tb}, \text{Ho}$. Thus it allows us to lean in favor of the "weak magnetic sublattice" MCE model [9], giving a qualitative interpretation of the magnetocaloric phenomena in the $\text{R}(\text{Me-Fe})_2$ intermetallic compounds with Laves phases structure.

These data prompted us to undertake the magnetic and magnetocaloric properties studies of similar to

mentioned - $\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ system with Fe content (x) from 0 to 0.60. These compounds, unlike those described above with iron concentration absence do not have a Curie point close to room temperature. However, they are of scientific interest from the point of view of the influence of cobalt replacement by iron on the Curie temperature, the magnitude and MCE peak width and refrigerating capacity (q) of these compounds.

2 Experimental details

$\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ alloys were melted in an electric arc furnace under a pure helium protection. An excess of rare earths metal (~ 3 wt. %) was added to the starting compositions the formation preventing of Co-rich phases. A homogenizing annealing of alloys was made in a vacuum furnace at 800 K during 24 hours. The samples structure was determined by X-ray diffraction technique (D8 Advance, Bruker) with $\text{Cu K}\alpha$ radiation source. Diffraction patterns were analyzed by Rietveld method using the "Fullprof" software [10].

Magnetic susceptibility temperature dependence measurements of the samples were carried out in an alternating magnetic field of 50 Oe in the temperature range from 25 to 800° C.

Their magnetization was measured using vibrating sample magnetometer (7407, Lake Shore Cryotronics) in the temperature range from 300 K to 850 K under a magnetic field up to 17 kOe.

3 Results

3.1 Properties of $\text{Gd}(\text{Co-Fe})_2$

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Analysis of the X-ray diffraction data at room temperatures showed that all samples contain mainly the 1:2 type Laves phase. Their crystal lattices belong to the $Fd\bar{3}m$ space group. For example, figure 1 shows the X-ray diffraction pattern at room temperatures for GdCo_2 .

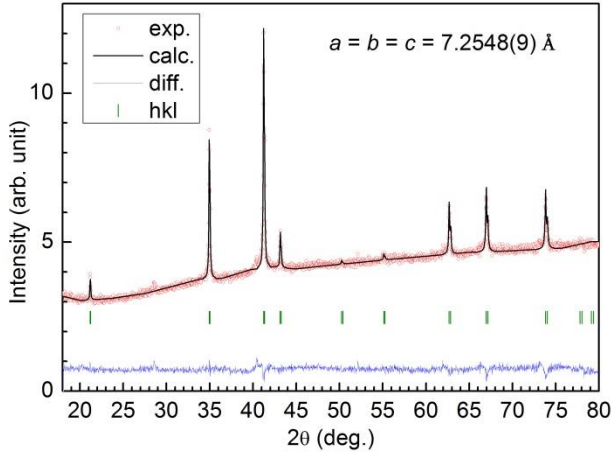


Fig. 1. The X-ray diffraction pattern of GdCo_2 .

Also, samples were confirmed to contain only 1:2-phase by measurements of susceptibility temperature dependences ($\chi(T)$) at external magnetic fields of $H = 50$ Oe. Curie temperatures (T_C) were determined from the positions of the dM/dT peaks on the magnetization (M) temperature axis, taken from the specific magnetization temperature dependencies ($M(T)$) in the magnetic field of 900 Oe (see Fig. 2).

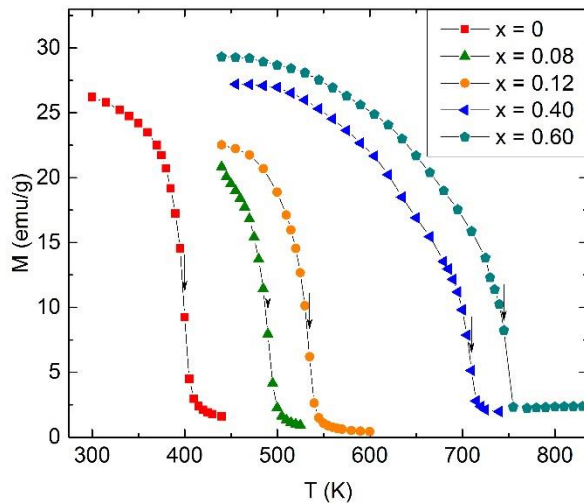


Fig. 2. Specific magnetization temperature dependences of $\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ intermetallic compounds in external magnetic field of 900 Oe. Arrow indicates the T_C point.

Figure 3 shows the field dependences of the specific magnetization at different temperatures for the $\text{Gd}(\text{Co}_{0.60}\text{Fe}_{0.40})_2$ compound. Similar isotherms are observed for the samples of other compounds. It can be seen that even at $T = 485$ K, that is only of 225 K below T_C , the magnetization curve practically reaches the saturation. This indirectly indicates that in this temperature range the compound has a low

magnetocrystalline anisotropy (MCA) energy and the relatively high degree of magnetic order is realized in Gd- sublattice. Consequently, the probability of the MCE appearance caused by the suppression of Gd atomic magnetic moments disorientation by an external magnetic field is small.

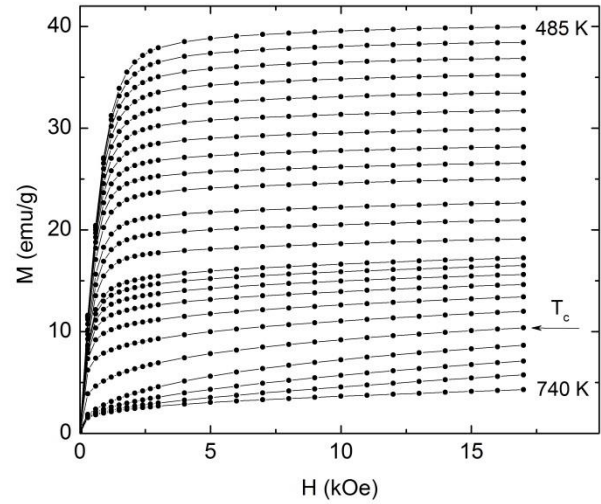


Fig. 3. Magnetization isotherms at various temperatures for the studied $\text{Gd}(\text{Co}_{0.60}\text{Fe}_{0.40})_2$ compound.

For the calculation of isothermal magnetic entropy change (ΔS_m), from the field magnetization $M(H)$ isotherms (Fig. 3), we used the following equation [11]:

$$\Delta S_m(H, T) = \int_0^H \left(\frac{\partial M(H, T)}{\partial T} \right)_H dH \quad (1)$$

In the case of a discrete temperature numbers and magnetic field values it takes the form:

$$\Delta S_m(H, T) = \sum_i \frac{M_{i+1}(T_{i+1}, H) - M_i(T_i, H)}{T_{i+1} - T_i} \Delta H. \quad (2)$$

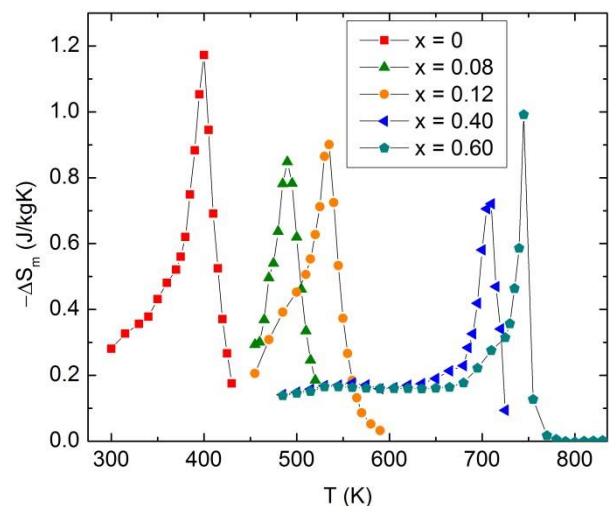


Fig. 4. Temperature dependences of magnetic entropy change $\Delta S_m(T)$ in magnetic fields (0-17) kOe for the studied $\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ compounds.

Figure 4 shows the calculated values of ΔS_m when the change of magnetic field $\Delta H = 17$ kOe. It can be seen

that, in contrast to the previously studied $R(\text{Co-Fe})_2$ compounds, where $R = \text{Dy, Ho, Er}$ [6, 7], for the samples with $R = \text{Gd}$, an ordinary symmetrical peak of $\Delta S_m(T)$ in T_C neighborhoods is observed.

Using the $\Delta S_m(T)$ data, we calculated the refrigerant capacity (q) [11]:

$$q = - \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_m(T) dT. \quad (3)$$

This parameter is used for comparison of the different magnetocaloric materials from the practical applications point of view. Values of q are presented in Table 1. Also the values of ΔT_{FWHM} , characterizing the distance between the highest and the lowest temperatures at the half maximum of the $-\Delta S(T)$ peak, are presented in this Table as well.

Table 1. The data on the temperature Curie (T_C), the refrigerating capacity parameter (q), the difference between the maximum and minimum temperatures at the half of ΔS_m maximum height (ΔT_{FWHM}) and maximum magnetic entropy change $-\Delta S_{\text{max}}$, of the studied $\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ samples at 15 kOe.

$\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$	T_C , K	q , J/kg	ΔT_{FWHM} , K	$-\Delta S$, J/kgK
$x = 0$	400	30	35	1.06
$x = 0.08$	490	23	35	0.78
$x = 0.12$	535	41	45	0.82
$x = 0.40$	710	18	30	0.72
$x = 0.60$	745	15	20	0.89

Consideration of the studied $\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ compounds under the practical perspective does not cause much enthusiasm: they have small values of ΔS -effect – 1 vs 5 J/kgK for Gd (at 17 and 20 kOe, respectively), and hardly can be considered as candidate materials for the manufacture of the working bodies in the magnetic refrigeration systems.

3.2 Comparison of $\text{Gd}(\text{Co-Fe})_2$ with $\text{Gd}(\text{Ni-Fe})_2$

Figure 5 presents the relative ΔS_m temperature dependence of $\text{Gd}(\text{Me}_{0.88}\text{Fe}_{0.12})_2$ ($\text{Me} = \text{Co, Ni}$) samples, where the ΔT_{FWHM} value characterizes the MCE peak width [1]. The grey and shaded areas (Fig. 5) correspond to the region of integration at q calculation. These data are 220 J/kg and 41 J/kg at $\Delta H = 15$ kOe for compounds with Ni and Co respectively. It can be seen from the figure that the compound with Ni has a plate-like $\Delta S_m(T)$ dependence while the compound with Co has a MCE peak in the vicinity of T_C typical for many ferromagnets. Hence this large difference in the MCE temperature dependences for the $\text{Gd}(\text{Me}_{0.88}\text{Fe}_{0.12})_2$ compounds with different Me is a consequence of a strong exchange interactions change in these compounds when Ni is replaced by Co.

Figure 6 shows the relative temperature dependences of the paramagnetic susceptibility - $\chi(T)$ of the studied compounds. The χ values were calculated from the linear parts of the $M(H)$ curves at the 10÷15 kOe magnetic fields range ($\chi = dM/dH$). It can be seen that the $\chi(T)$ dependence for the compound with Ni in the below T_C region lies significantly higher than for the compound with Co (the difference between the curves is shaded); For the sample with Co the $\chi(T)$ growth with T rise is much faster. These differences in the $\chi(T)$ variation is an indirect confirmation of the much higher disorder degree in Gd –sublattice for the samples with Ni due to the weaker exchange interaction between Gd and 3d ions sublattices.

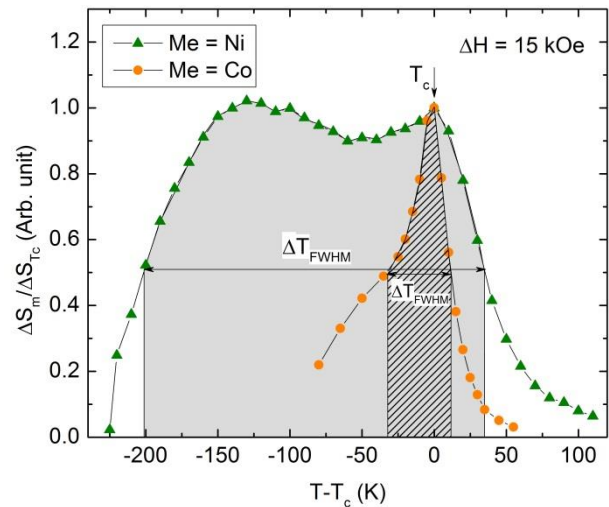


Fig. 5. Relative MCE temperature dependence of $\text{Gd}(\text{Me}_{0.88}\text{Fe}_{0.12})_2$, where $\text{Me} = \text{Co, Ni}$.

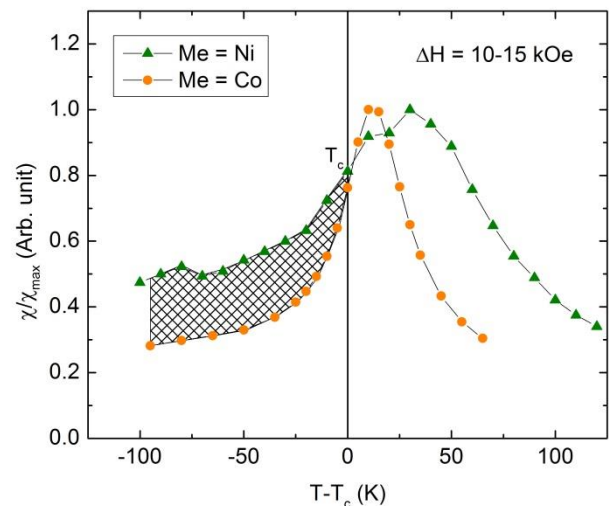


Fig. 6. Temperature dependencies of the relative paramagnetic susceptibility - $\chi(T)$ on the Me-type in $\text{Gd}(\text{Me}_{0.88}\text{Fe}_{0.12})_2$ compounds, where $\text{Me} = \text{Co, Ni}$.

4 Conclusions

Thus, the magnetic and magnetocaloric properties study of the $\text{Gd}(\text{Co}_{1-x}\text{Fe}_x)_2$ ($x = 0, 0.08, 0.12, 0.40, 0.60$) compounds revealed the following:

In these compounds no broadening of the MCE peak observed contrary to that for such compounds with heavier $R = \text{Tb, Dy, Ho, Er}$ [5, 6];

In contrast to the isostructural $\text{Gd}(\text{Ni-Fe})_2$ intermetallics, where the magnetic entropy $-\Delta S_m(T)$ and paraprocess susceptibility $-\chi(T)$ maxima broadenings are observed, in the given compounds, apparently much stronger internal and inter-sublattice exchange interactions keep the magnetic order in both sublattices in the higher degree almost for the whole $0 \text{ K} \div T_C$ temperature interval. So such narrow peaks on $\Delta S_m(T)$ and $\chi(T)$ dependences appear only in the vicinity of T_C point.

The obtained results are important for understanding the nature of magnetic and magnetocaloric properties of the large $R(\text{Co}_{1-x}\text{Fe}_x)_2$ Laves phases group as a whole.

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